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Frame-invariant Fick diffusion matrices of multicomponent fluid mixtures

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Extension of a description of mass diffusion in binary fluids based on Fick's law to multicomponent fluids requires introduction of diffusion matrices. A problem is that Fick diffusion matrices commonly adopted for multicomponent fluids depend on the velocity frame of reference. In this paper we show how one can define Fick diffusion matrices for multicomponent fluids that are frame invariant.

1 Introduction

Diffusion in multicomponent fluid mixtures is a ubiquitous phenomenon in nature and in technical applications. While diffusion in binary mixtures is well understood, a better understanding of diffusion in multicomponent fluids is still desirable, in particular regarding cross-diffusion coefficients and their dependence on reference frames. For this reason there are currently extensive efforts, involving several research groups, for an accurate characterization of diffusion coefficients (including cross-diffusion) for selected liquid mixtures, starting with ternary mixtures as a stepping stone towards fully multicomponent fluid mixtures.^{1–5}

Because of the phenomenon of cross-diffusion,⁶ the description of mass diffusion in multicomponent mixtures is qualitatively different from the simpler case of a binary mixture. Even in the case of isotropic mixtures, to be considered in the present paper, the mathematical description of diffusion requires diffusion matrices. A major complication is that the actual values of coefficients in diffusion matrices based on Fick's law depend upon the representation used to specify the composition of the mixture, *i.e.*, whether mass fractions, mole fractions or volume fractions are used. As will be discussed in Section 2, a specific choice of concentration representation correlates with a specific frame of reference for the definition of diffusion fluxes. This frame dependence of the diffusion coefficients does not exist in isotropic binary mixtures, for which a single coefficient has the same numerical value, regardless of the concentration representation adopted. But the frame dependence

of Fick diffusion matrices introduces complexity and confusion in diffusion research in multicomponent mixtures. Sometimes authors do not specify the frame of reference adopted in reporting experimental data and leave it up to the reader to infer the frame of reference from the experimental technique used to get the diffusion-coefficient data.^{7–9} A detailed analysis of the complexities associated with the frame dependence of the diffusion matrices in ternary mixtures has recently been reported by Svetsova and coworkers.¹⁰

Some of the problems associated with Fick diffusion matrices may be alleviated by adopting the Maxwell–Stefan approach to diffusion in multicomponent mixtures.^{6,11–15} Maxwell–Stefan diffusion matrices relate chemical-potential gradients to differences between velocities of the components and the resulting diffusion matrices do not depend on a reference frame.^{13–15} Nevertheless, Fick's approach to diffusion is most popular in experiments, because chemical potentials in a multicomponent mixture can only be obtained indirectly, while concentrations allow for direct measurement. Fick's approach also combines more naturally with mass balance in multicomponent fluid flow.^{16,17}

The problem of frame dependence, similar to the one appearing in Fick's approach for isothermal diffusion, is also encountered in the case of thermodiffusion.¹⁸ In the case of thermodiffusion, the issue already requires a specific frame-independent definition of the thermodiffusion coefficient D_T or Soret coefficient S_T for binary mixtures. In a previous paper one of us has shown how the procedure for binary mixtures can be generalized to obtain frame-independent thermodiffusion coefficients of multicomponent mixtures.¹⁹ In the present paper we consider the case of isothermal diffusion that was not considered in the previous paper. Specifically, we shall show how a simple similarity transformation of frame-dependent Fick diffusion matrices yields Fick diffusion matrices that are indeed independent of the reference frame.

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We have organized this paper as follows. First and for completeness, we start in Section 2 by reviewing different frames of references and corresponding diffusion fluxes. Then, in Section 3, we review Fick's diffusion in binary mixtures, emphasizing the frame independence of the single diffusion coefficient D . We then proceed to consider in Section 4 the case of a ternary mixture, which represents the first type of mixture where the complications associated with frame dependence of Fick's diffusion matrices first appears, followed by an analysis of binary limits in Section 5. In Section 6 we make some comments on the composition dependence of frame-dependent *versus* frame-independent diffusion matrices for a particular example of a ternary mixture. In Section 7 we show how the procedure, specified in detail for ternary mixtures, can be readily generalized to multicomponent mixtures. In Section 8 we show how the results of the present paper for isothermal diffusion can be extended to the general case of non-isothermal diffusion. Our conclusions are summarized in Section 9.

2 Diffusion fluxes

This paper is primarily concerned with isothermal diffusion caused by the presence of a concentration gradient. Comments on thermodiffusion resulting from the presence of a temperature gradient will be added at the end of the paper. Diffusion appears because, in general, in a multicomponent mixture different components i move with different velocities \mathbf{u}_i . The diffusion flux \mathbf{J}_i of component i is generally defined as proportional to the difference between the velocity \mathbf{u}_i and some average velocity. Depending on the choice adopted for the average velocity, different diffusion fluxes can be defined, namely, relative to the average molar velocity, the barycentric velocity, or the average volume velocity. The following three diffusion fluxes are most used in practice:⁶

(1) Mass diffusion flux relative to the center of mass velocity:

$$\mathbf{J}_i^w = \rho_i \left[\mathbf{u}_i - \left(\sum_j w_j \mathbf{u}_j \right) \right] \quad (1)$$

in terms of SI units of $\text{kg m}^{-2} \text{s}^{-1}$. Here ρ_i is the mass density of component i (kg m^{-3}) and $w_i = \rho_i / \rho_t$ the corresponding mass fraction with $\rho_t = \sum_j \rho_j$ the total mass density. In this paper we

adopt the convention that the summation is over all components of the mixture unless indicated otherwise.

(2) Molar diffusion flux relative to the center of molar velocity:

$$\mathbf{J}_i^x = c_i \left[\mathbf{u}_i - \left(\sum_j x_j \mathbf{u}_j \right) \right] \quad (2)$$

in terms of SI units of $\text{mol m}^{-2} \text{s}^{-1}$. Here c_i is the molar concentration of component i (mol m^{-3}) and $x_i = c_i / c_t$ the corresponding mole fraction with $c_t = \sum_j c_j$ the total molar density (equal to the inverse molar volume).

(3) Molar diffusion relative to the center of volume velocity:

$$\mathbf{J}_i^V = c_i \left[\mathbf{u}_i - \left(\sum_j \phi_j \mathbf{u}_j \right) \right] \quad (3)$$

in terms of SI units of $\text{mol m}^{-2} \text{s}^{-1}$. Here $\phi_i = x_i \hat{V}_i / \sum_j x_j \hat{V}_j$ is the volume fraction of component i , where \hat{V}_i is the partial molar volume of component i . The total molar volume is $\hat{V} = \sum_j x_j \hat{V}_j$ (equal to the inverse total molar concentration).

For the purpose of this paper it is important to distinguish among the different diffusion fluxes and properties defined in the different reference frames, for which we use roman superscripts, w, x, or V, as we did in the equations above. According to eqn (1)–(3), one can define for each reference frame as many diffusion fluxes as the number of components n in the mixture. However, only $n - 1$ of these fluxes are independent, since:⁶

$$\sum_i \mathbf{J}_i^w = 0, \quad \sum_i \mathbf{J}_i^x = 0, \quad \sum_i \mathbf{J}_i^V = 0 \quad (4)$$

Note that $c_t^{-1} = \sum_j x_j \hat{V}_j$.

3 Isothermal Fick diffusion in binary mixtures

In an binary mixture there is only one independent concentration, such as a mass fraction w or a mole fraction x , and, in accordance with eqn (4), one single independent diffusion flux. Upon solving eqn (1) and (2) for $\mathbf{u}_1 - \mathbf{u}_2$, the relationship between the single independent mass diffusion flux (e.g., $\mathbf{J}^w = \mathbf{J}_1^w$) and the single independent molar diffusion flux (e.g., $\mathbf{J}^x = \mathbf{J}_1^x$) is readily expressed as:^{6,19}

$$\frac{\mathbf{J}^w}{\rho_t w(1-w)} = \frac{\mathbf{J}^x}{c_t x(1-x)} \quad (5)$$

In nonequilibrium thermodynamics^{13,20,21} Fick's law postulates a linear relationship between the mass flux and the gradient of mass fraction or the molar diffusion flux and the gradient of mole fraction. For isotropic binary mixtures:

$$\begin{aligned} \mathbf{J}^w &= -\rho_t D \nabla w, \\ \mathbf{J}^x &= -c_t D \nabla x. \end{aligned} \quad (6)$$

For the purpose of the present paper it is important to note that, in a binary mixture, the relationship between the gradient of mass fraction and the gradient of mole fraction can be expressed as^{6,19,22}

$$\frac{\nabla w}{w(1-w)} = \frac{\nabla x}{x(1-x)} \quad (7)$$

From eqn (5) and (7) it follows that the two relations in eqn (6) are perfectly consistent, i.e., the single scalar diffusion coefficient D of an isotropic binary mixture is invariant under change from

the barycentric frame of reference of eqn (1) to the center of molar-velocity frame of reference of eqn (2).

This is also true for the volume frame of reference. On the one hand, upon solving eqn (2) and (3) for $\mathbf{u}_1 - \mathbf{u}_2$, the relationship between the different diffusion fluxes can be expressed as⁶

$$\frac{\mathbf{J}_1^V}{x(1-\phi)} = \frac{\mathbf{J}^x}{x(1-x)} = \frac{-\mathbf{J}_2^V}{\phi(1-x)}, \quad (8)$$

where use has been made of the relation between molar concentrations and molar fractions, namely, $c_1 = x c_t$ and $c_2 = (1-x)c_t$. On the other hand, the relationship between gradients in molar concentration and mole fraction of component 1 for a binary mixture can be expressed as⁶

$$\begin{aligned} \nabla c_1 &= \frac{\hat{V}_2}{\hat{V}} \nabla x = \frac{1-\phi}{1-x} c_t \nabla x, \\ \nabla c_2 &= -\frac{\hat{V}_1}{\hat{V}} \nabla x = -\frac{\phi}{x} c_t \nabla x. \end{aligned} \quad (9)$$

Upon substituting both eqn (8) and (9) into eqn (6), one readily obtains Fick's law in the volume frame of reference:

$$\begin{aligned} \mathbf{J}_1^V &= -D \nabla c_1, \\ \mathbf{J}_2^V &= -D \nabla c_2, \end{aligned} \quad (10)$$

with the same diffusion coefficient D that appears in eqn (6).

The consistency of eqn (6) and (10) confirms the frame invariance of isothermal Fick's diffusion in a binary mixture. This is an important property from a practical point of view. It makes dealing with isothermal Fick diffusion in binary mixtures simpler, whether theoretically,²⁰ experimentally,^{1,3,4,7,8,23} or by numerical simulations.^{24,25} Thus scientists can continue to use their preferred concentration representation, either mass fraction,^{1,4,5,20} mole fraction,^{7,8,24,25} or molar concentration^{23,26} without a need for inconvenient conversion to compare values reported for the diffusion coefficient of binary mixtures.

Eqn (6) and (10) also show how each reference frame for the definition of diffusion fluxes naturally correlates with a specific concentration representation, either mass fraction, mole fraction, or molar concentration.

4 Isothermal Fick diffusion in ternary mixtures

In ternary mixtures, in accordance with eqn (4), there are two independent diffusion fluxes and, associated with them, two independent concentration gradients. A description of isothermal diffusion by Fick's law assumes all components to be equal, so that a given diffusion flux depends linearly on all independent concentration gradients. In the barycentric frame of reference, the first relation in eqn (6) is usually extended to a ternary mixture by writing⁶

$$\begin{pmatrix} \mathbf{J}_1^w \\ \mathbf{J}_2^w \end{pmatrix} = -\rho_t D^w \cdot \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix} \quad (11)$$

with

$$D^w = \begin{bmatrix} D_{11}^w & D_{12}^w \\ D_{21}^w & D_{22}^w \end{bmatrix}, \quad (12)$$

the Fick diffusion matrix in the barycentric frame of reference. In the center of molar-velocity frame of reference, one expresses Fick's law with concentrations in terms of mole fraction and, similarly to the second relation in eqn (6) for binary mixtures, one writes for a ternary mixture

$$\begin{pmatrix} \mathbf{J}_1^x \\ \mathbf{J}_2^x \end{pmatrix} = -c_t D^x \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix}. \quad (13)$$

with the corresponding Fick diffusion matrix in the center of molar-velocity frame of reference

$$D^x = \begin{bmatrix} D_{11}^x & D_{12}^x \\ D_{21}^x & D_{22}^x \end{bmatrix}. \quad (14)$$

In contrast to a binary mixture where there is a single (scalar) diffusion coefficient, in ternary mixtures $D^w \neq D^x$. As mentioned in the introduction, this frame dependence of diffusion matrices has caused some difficulties in practice, when dealing with experimental data or numerical simulations.^{4,10} In this paper we propose a redefinition of Fick diffusion matrices that will eliminate this difficulty. In doing so, we build on a concept previously applied to thermodiffusion in ternary mixtures, where it was shown that the relationship between properties in the mass and in the molar frame of reference is easily expressed by introducing "concentration" matrices defined by¹⁹

$$X = \begin{bmatrix} x_1(1-x_1) & -x_1x_2 \\ -x_1x_2 & x_2(1-x_2) \end{bmatrix}, \quad (15)$$

and

$$W = \begin{bmatrix} w_1(1-w_1) & -w_1w_2 \\ -w_1w_2 & w_2(1-w_2) \end{bmatrix}. \quad (16)$$

In terms of these concentration matrices, the two gradients in mass fraction and the two gradients in mole fraction can be related by an expression that resembles eqn (7) for binary mixtures:

$$X^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix} = W^{-1} \cdot \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix}. \quad (17)$$

From eqn (1) and (2) it can be shown that the two fluxes in the mole frame of reference are related to the two fluxes in the mass frame of reference by an expression that resembles eqn (5) for binary mixtures:

$$\begin{pmatrix} \mathbf{J}_1^w \\ \mathbf{J}_2^w \end{pmatrix} = \frac{\rho_t}{c_t} W \cdot X^{-1} \cdot \begin{pmatrix} \mathbf{J}_1^x \\ \mathbf{J}_2^x \end{pmatrix}. \quad (18)$$

Next, by combining eqn (17) and (18) with eqn (11) and (13), one readily obtains¹⁹

$$W^{-1} \cdot D^w \cdot W = X^{-1} \cdot D^x \cdot X \equiv D, \quad (19)$$

which defines a frame-independent diffusion matrix D . Of course, use of this frame-independent diffusion matrix D implies a change of the actual formulation of Fick's law. In terms of the frame-independent diffusion matrix D , Fick's law in the mass frame of reference now reads:

$$\begin{pmatrix} J_1^w \\ J_2^w \end{pmatrix} = -\rho_t W \cdot D \cdot W^{-1} \cdot \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix}, \quad (20)$$

while in the center of molar-velocity frame of reference Fick's law now reads:

$$\begin{pmatrix} J_1^x \\ J_2^x \end{pmatrix} = -c_t X \cdot D \cdot X^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix}. \quad (21)$$

The advantage of this formulation of Fick's law is that exactly the same invariant diffusion matrix D appears in eqn (20) and in eqn (21). Notice from eqn (20) and (21) above that in the case of a binary mixture the product is commutative, so that the prefactors before and after the diffusion coefficient D cancel and we recover Fick's law in its traditional form as given by eqn (6).

The ideas above can also be extended to include the volume frame of reference. In the case of the volume frame of reference we introduce a third concentration matrix defined by

$$\Phi = \begin{bmatrix} x_1(1 - \phi_1) & -x_1\phi_2 \\ -\phi_1x_2 & x_2(1 - \phi_2) \end{bmatrix}. \quad (22)$$

From eqn (2) and (3) it readily follows that for a ternary mixture

$$\Phi^{-1} \cdot \begin{pmatrix} J_1^v \\ J_2^v \end{pmatrix} = X^{-1} \cdot \begin{pmatrix} J_1^x \\ J_2^x \end{pmatrix}, \quad (23)$$

which represents the generalization of eqn (8) to a ternary mixture. Similarly to the role of matrices W and X , the matrix Φ is convenient for relating gradients of mole fraction to the gradients of molar concentration. Indeed differentiation of the expression of molar concentration as a function of mole fraction yields:

$$\begin{pmatrix} \nabla c_1 \\ \nabla c_2 \end{pmatrix} = c_t \Phi \cdot X^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix}. \quad (24)$$

To obtain eqn (24) one needs to consider $c_1 = x_1 c_t$ and $c_2 = x_2 c_t$ and the expression of the molar volume of a ternary mixture:

$$\hat{V} = x_1 \hat{V}_1 + x_2 \hat{V}_2 + x_3 \hat{V}_3 = c_t^{-1}. \quad (25)$$

In addition, one has to use the following thermodynamic relations linking the derivatives of the three partial molar volumes \hat{V}_i of a ternary mixture:

$$\begin{aligned} x_1 \frac{\partial \hat{V}_1}{\partial x_1} + x_2 \frac{\partial \hat{V}_2}{\partial x_1} + (1 - x_1 - x_2) \frac{\partial \hat{V}_3}{\partial x_1} &= 0, \\ x_1 \frac{\partial \hat{V}_1}{\partial x_2} + x_2 \frac{\partial \hat{V}_2}{\partial x_2} + (1 - x_1 - x_2) \frac{\partial \hat{V}_3}{\partial x_2} &= 0, \end{aligned} \quad (26)$$

which apply when x_1 and x_2 are adopted as the two independent concentration variables and $x_3 = 1 - x_1 - x_2$.

Next, upon combining eqn (23) and (24) with Fick's law in the center of molar-velocity frame of reference, as given by eqn (21), we obtain in terms of the frame-invariant diffusion matrix D :

$$\begin{pmatrix} J_1^v \\ J_2^v \end{pmatrix} = -\Phi \cdot D \cdot \Phi^{-1} \cdot \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \end{pmatrix}, \quad (27)$$

which is the natural generalization of eqn (9) for a binary mixture to a ternary mixture, and is consistent with eqn (20) or eqn (21). Note that the invariant Fick diffusion matrix D in eqn (27) for the molar diffusion fluxes relative to the center of volume velocity is identical to the one in eqn (20) for the mass diffusion fluxes relative to the center of mass velocity, and in eqn (21) for the molar diffusion fluxes relative to the center of molar velocity. Hence, we have indeed been able to formulate Fick's law for a ternary mixture in the three most useful frames of references in terms of a single invariant diffusion matrix D by applying a simple elegant similarity transformation. As a corollary to eqn (27), its combination with eqn (19) yields

$$W^{-1} \cdot D^w \cdot W = X^{-1} \cdot D^x \cdot X = \Phi^{-1} \cdot D^v \cdot \Phi = D, \quad (28)$$

where D^v is the Fick diffusion matrix in the volume-average frame of ref. 6. Eqn (28) provides an alternative way of presenting the relation between Fick diffusion matrices in different reference frames, which in some circumstances may be advantageous compared with the more traditional way, as found, *e.g.*, in the book of Taylor and Krishna.⁶

There are some differences between the matrix Φ on the one hand and the matrices W and X on the other hand that are relevant from a practical point of view. Since laboratory mixtures are typically prepared by weight, the matrices W and X are commonly known. However, a full knowledge of the matrix Φ requires equations of state for the partial molar volumes \hat{V}_i . We also note that the matrices W and X are symmetric, while the matrix Φ is not.

We conclude this section with some comments on the advantages and disadvantages of frame-invariant Fick diffusion matrices *versus* frame-invariant Maxwell–Stefan diffusion matrices. Maxwell–Stefan diffusion matrices relate diffusion fluxes to chemical potential gradients.^{11–14} They are convenient for molecular dynamics simulations, since they are related to time-dependent correlation functions.^{14,24,25} Another advantage of Maxwell–Stefan matrices is that they are symmetric, while the frame-invariant Fick diffusion matrices D are not. However, the frame-invariant Fick diffusion matrices are directly related to the concentrations and concentration gradients that are more easily accessible experimentally. Hence, we believe that the frame-invariant Fick diffusion matrices, introduced in this paper, will be more convenient in practice for the interpretation and intercomparison of experimental diffusion data. The relations between Maxwell–Stefan diffusion matrices and frame-dependent Fick diffusion matrices D^w and D^x have been discussed in the literature.^{14,24,27} Of course, to relate

Maxwell–Stefan diffusion matrices to the frame-invariant Fick diffusion matrices an additional similarity transformation in accordance with eqn (19) is required.

5 Binary limits of ternary mixtures

For dealing with diffusion in ternary mixtures it is useful to discuss the diffusion matrices in the three binary-component limits, that is, at the sides of the ternary concentration triangle, where one of the concentrations is dilute. For diffusion matrices in the barycentric frame of reference the limiting relations are given by:^{5,28}

$$\begin{aligned} \text{when } x_1 \rightarrow 0, & \begin{cases} D_{22}^w \rightarrow D_{\text{bin}}^{(23)} \\ D_{12}^w \rightarrow 0 \end{cases}, \\ \text{when } x_2 \rightarrow 0, & \begin{cases} D_{11}^w \rightarrow D_{\text{bin}}^{(13)} \\ D_{21}^w \rightarrow 0 \end{cases}, \\ \text{when } x_3 \rightarrow 0, & \begin{cases} D_{22}^w \rightarrow D_{21}^w \rightarrow D_{\text{bin}}^{(12)} \\ D_{11}^w + D_{21}^w - D_{12}^w - D_{22}^w \rightarrow 0 \end{cases}, \end{aligned} \quad (29)$$

where $D_{\text{bin}}^{(ij)}$ represents the diffusion coefficient in the binary mixture with components i and j . In a binary mixture the single diffusion coefficient $D_{\text{bin}}^{(ij)}$ is frame independent, so no further notation is needed. Since some of the diffusion coefficients in ternary mixtures are typically measured with much higher accuracy than others, eqn (29) turn out to be useful in practice.⁵ It is, therefore, interesting to find the corresponding limits for the frame-invariant diffusion matrix D defined by eqn (19). Combining eqn (29) and (19) with the explicit expressions, eqn (15) and (16), of the concentration matrices, one finds after some algebra:

$$\begin{aligned} \text{when } x_1 \rightarrow 0, & \begin{cases} D_{22} \rightarrow D_{\text{bin}}^{(23)} \\ D_{12} \rightarrow 0 \end{cases}, \\ \text{when } x_2 \rightarrow 0, & \begin{cases} D_{11} \rightarrow D_{\text{bin}}^{(13)} \\ D_{12} \rightarrow 0 \end{cases}, \\ \text{when } x_3 \rightarrow 0, & \begin{cases} D_{11} - D_{21} \rightarrow D_{\text{bin}}^{(12)} \\ D_{11} - D_{21} + D_{12} - D_{22} \rightarrow 0 \end{cases}. \end{aligned} \quad (30)$$

It is interesting to compare the binary limits (29) of the frame-dependent diffusion matrices with the binary limits (30) of the frame-independent diffusion matrix. The limits for the main diffusivities are similar, whereas cross-diffusivities show different behaviors. For instance, in the limit $x_1 \rightarrow 0$ the frame-dependent cross-diffusivity D_{12}^w must vanish, while in the same

limit it is the frame-independent cross-diffusivity D_{21} that vanishes.

6 Composition dependence of Fick diffusion matrices

As is the case for thermodiffusion coefficients in binary mixtures,^{18,29} one may expect that in mixtures of weakly interacting components the concentration prefactors in our formulation of Fick's law may carry a significant part of the composition dependence, so that the frame-invariant diffusion matrix D in eqn (28) could become less dependent on concentration than the corresponding Fick diffusion matrices in the various reference frames.

Obviously, a detailed clarification of this issue requires an extensive and thorough investigation. However, for the sake of a simple illustration, we have analyzed the extensive data set obtained by Sechenyh *et al.*, who measured the diffusion matrix in the barycentric frame of reference for the mixture 1,2,3,4-tetrahydronaphthalene + isobutylbenzene + *n*-dodecane at 20 different compositions.⁵ For each of the experimental compositions we have evaluated the corresponding frame-invariant diffusion matrix D defined by eqn (19). The results of this analysis for the cross-diffusivities are displayed as ternary contour plots in Fig. 1. The left column shows the plots for the barycentric cross-diffusivities D_{12}^w and D_{21}^w reported by Sechenyh *et al.* The right column shows the corresponding frame-independent cross-diffusivities obtained from eqn (19). Note that the color scheme is the same for the plots in the left and right columns. One sees that the intermediate greenish colors dominate in larger areas in the plots in the right column, while the contour curves are generally more separated, indicating that composition dependence is less important for the frame-invariant diffusivities. In particular, the two local minima appearing in the plots of D_{12}^w and D_{21}^w do not show up in their corresponding frame-independent counterparts. Note also that in the frame invariant cases the limits of eqn (30) are very smoothly approached, either at $w_1 \rightarrow 0$ for D_{21} or at $w_2 \rightarrow 0$ for D_{12} .

7 Isothermal Fick diffusion in multicomponent mixtures

For simplicity we started by formulating frame-invariant Fick diffusion matrices in detail for ternary mixtures in Section 4. However, the procedure can be readily extended to mixtures with an arbitrary number of components. For this purpose we consider $(n - 1) \times (n - 1)$ matrices X , W , and Φ with matrix elements defined by

$$X_{ij} = x_i \delta_{ij} - x_i x_j, \quad W_{ij} = w_i \delta_{ij} - w_i w_j, \quad \Phi_{ij} = x_i \delta_{ij} - \phi_j x_i. \quad (31)$$

Here $i, j \in \{1, n - 1\}$ are the independent components, while x_n , w_n , or ϕ_n are the dependent concentrations, and where δ_{ij} are Kronecker deltas. Then a little bit of algebra shows that eqn (17)

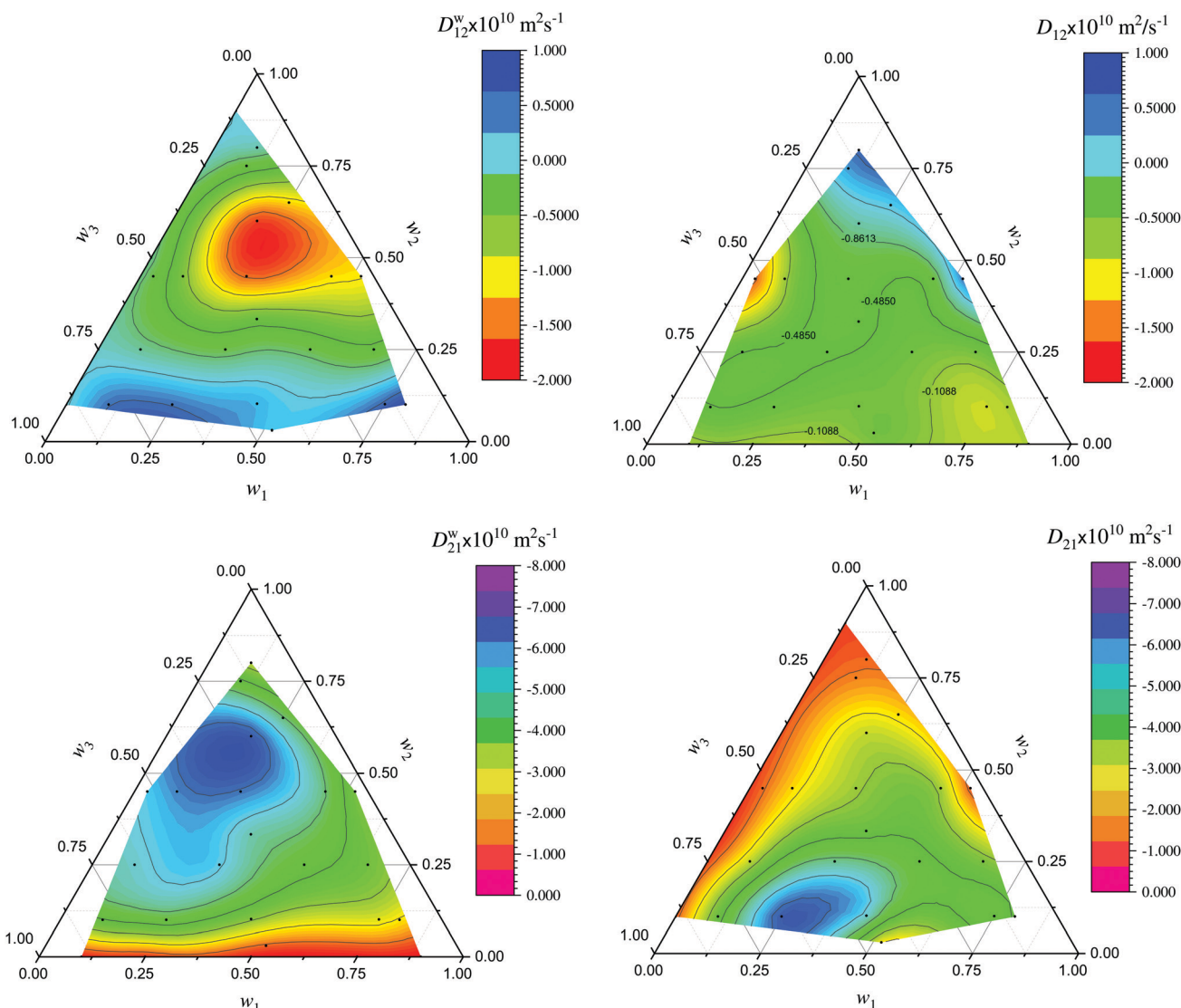


Fig. 1 Ternary contour plots of the frame-dependent cross-diffusivities D_{12}^w and D_{21}^w (left column) for a mixture of 1,2,3,4-tetrahydronaphthalene + isobutylbenzene + *n*-dodecane reported by Sechenyh *et al.*,⁵ and the corresponding frame-independent cross-diffusivities D_{12} and D_{21} obtained from eqn (19). The binary limits, given by eqn (29) or eqn (30), have been used to complement the experimental data in each case.

holds in general:

$$\mathbf{X}^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \\ \vdots \\ \nabla x_{n-1} \end{pmatrix} = \mathbf{W}^{-1} \cdot \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \\ \vdots \\ \nabla w_{n-1} \end{pmatrix}. \quad (32)$$

Similarly, eqn (24) for molar concentrations also holds in general:

$$\Phi^{-1} \cdot \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \\ \vdots \\ \nabla c_{n-1} \end{pmatrix} = c_t \mathbf{X}^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \\ \vdots \\ \nabla x_{n-1} \end{pmatrix}. \quad (33)$$

The relations (18) and (23) between the diffusion fluxes in different reference frames generalize to:

$$\begin{pmatrix} \mathbf{J}_1^w \\ \mathbf{J}_2^w \\ \vdots \\ \mathbf{J}_{n-1}^w \end{pmatrix} = \frac{\rho_t \mathbf{W}}{c_t} \cdot \mathbf{X}^{-1} \cdot \begin{pmatrix} \mathbf{J}_1^x \\ \mathbf{J}_2^x \\ \vdots \\ \mathbf{J}_{n-1}^x \end{pmatrix}, \quad (34)$$

and

$$\begin{pmatrix} \mathbf{J}_1^v \\ \mathbf{J}_2^v \\ \vdots \\ \mathbf{J}_{n-1}^v \end{pmatrix} = \Phi \cdot \mathbf{X}^{-1} \cdot \begin{pmatrix} \mathbf{J}_1^x \\ \mathbf{J}_2^x \\ \vdots \\ \mathbf{J}_{n-1}^x \end{pmatrix}. \quad (35)$$

Hence, the $(n - 1) \times (n - 1)$ matrices X , W , and Φ can be used to define a frame-independent Fick diffusion matrix D for multicomponent mixtures just in the same way as was shown explicitly for ternary mixtures in Section 4. Specifically, the Fick's laws, given by eqn (20), (21) or (27) for ternary mixtures in Section 4, hold in general for an arbitrary number of components with a single frame-invariant diffusion matrix D :

$$\begin{pmatrix} J_1^w \\ J_2^w \\ \vdots \\ J_{n-1}^w \end{pmatrix} = -\rho_t W \cdot D \cdot W^{-1} \cdot \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \\ \vdots \\ \nabla w_{n-1} \end{pmatrix}, \quad (36)$$

$$\begin{pmatrix} J_1^x \\ J_2^x \\ \vdots \\ J_{n-1}^x \end{pmatrix} = -c_t X \cdot D \cdot X^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \\ \vdots \\ \nabla x_{n-1} \end{pmatrix}, \quad (37)$$

$$\begin{pmatrix} J_1^v \\ J_2^v \\ \vdots \\ J_{n-1}^v \end{pmatrix} = -\Phi \cdot D \cdot \Phi^{-1} \cdot \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \\ \vdots \\ \nabla c_{n-1} \end{pmatrix}. \quad (38)$$

As a corollary, eqn (28) continues to hold for an arbitrary number of components providing an alternative way of switching Fick diffusion matrices between different reference frames.

8 Non-isothermal diffusion in multicomponent mixtures

When diffusion is not isothermal, there is a thermodiffusion contribution proportional to the temperature gradient ∇T . When both a concentration gradient and a temperature gradient are present, the molar diffusion flux in a binary mixture has traditionally been expressed as^{13,21}

$$J^x = -c_t [D \nabla x + x(1 - x) D_T \nabla T], \quad (39)$$

while the mass diffusion flux is expressed as

$$J^w = -\rho_t [D \nabla w + w(1 - w) D_T \nabla T]. \quad (40)$$

Note the presence of the concentration prefactors, $x(1 - x)$ in eqn (39) and $w(1 - w)$ in eqn (40). They are used so that the thermodiffusion coefficient D_T has the same value in eqn (39) and in eqn (40). Essentially we have used the same concept in defining frame-independent Fick diffusion matrices in the contribution from the concentration gradient. In the previous paper, it has been shown how the thermodiffusion contribution proportional to the temperature gradient can be formulated for a multicomponent mixture in terms of $(n - 1)$ frame-independent thermodiffusion coefficients $D_{T,i}$ ($i \in 1, n - 1$).¹⁹

Combining the formulation developed for the Fick diffusion contribution in this paper with that for the thermodiffusion contribution, we thus obtain for a mixture of n components:

$$\begin{pmatrix} J_1^x \\ J_2^x \\ \vdots \\ J_{n-1}^x \end{pmatrix} = -c_t \left\{ X \cdot D \cdot X^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \\ \vdots \\ \nabla x_{n-1} \end{pmatrix} + X \cdot \begin{pmatrix} D_{T,1} \\ D_{T,2} \\ \vdots \\ D_{T,n-1} \end{pmatrix} \nabla T \right\}, \quad (41)$$

and

$$\begin{pmatrix} J_1^w \\ J_2^w \\ \vdots \\ J_{n-1}^w \end{pmatrix} = -\rho_t \left\{ W \cdot D \cdot W^{-1} \cdot \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \\ \vdots \\ \nabla w_{n-1} \end{pmatrix} + W \cdot \begin{pmatrix} D_{T,1} \\ D_{T,2} \\ \vdots \\ D_{T,n-1} \end{pmatrix} \nabla T \right\}. \quad (42)$$

9 Conclusions

We have shown, first for a ternary mixture and subsequently for a multicomponent mixture, how the diffusion resulting from a concentration gradient, can be expressed in terms of a Fick diffusion matrix D , defined by eqn (28), that is independent of the frame of reference. When combined with thermodiffusion resulting from a temperature gradient, we have obtained a formulation that contains both a frame-independent diffusion matrix D and $n - 1$ frame-independent thermodiffusion coefficients $D_{T,i}$ as shown in eqn (41) and (42).

Conflicts of interest

There are no conflicts of interest.

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